REPORT DOCUMENTATION PAGE

Form Approved OMB NO. 0704-0188

1. REPORT DATE (DD-MM-YYYY)	2. REPORT TYPE	3. DATES COVERED (From - To)
30-04-2015	Final Report	1-Feb-2014 - 31-Jan-2015

4. TITLE AND SUBTITLE

Final Report: Benchtop Transmission Electron Microscope (TEM) with Electron Diffraction (ED) and Scanning Electron Microscopy (SEM) Capabilities for Analysis of Inorganic Solution-Processed Flexible Solar Cells

5a. CONTRACT NUMBER
W911NF-14-1-0071

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER
206022

6. AUTHORS
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5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAMES AND ADDRESSES

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Dover, DE 19901 -2277

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS (ES)

U.S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSOR/MONITOR'S ACRONYM(S)
ARO

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
64755-EL-REP.1

12. DISTRIBUTION AVAILIBILITY STATEMENT

Approved for Public Release; Distribution Unlimited

13. SUPPLEMENTARY NOTES

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14. ABSTRACT

The award W911NF-14-1-0071 made to Delaware State University enabled the acquisition of a benchtop low-voltage Transmission Electron Microscope (TEM) with Scanning Electron Microscope (SEM) Capability: LV EM 5. The instrument acquisition supports Analysis of Inorganic Solution-Processed Flexible Solar Cells and has been used to accomplished the project objectives:
O1. Support the project "Novel Thin-Film Photovoltaic Technologies Using Solution Nano-Precursors to Cu2ZnSnS4, Fe2SiS4, and Fe2GeS4 Based Absorber Layers", research ongoing in Dr. Daniela Radu's (PI)

15. SUBJECT TERMS

Transmission Electron Microscope, Scanning Electron Microscope, nanoparticles, nanostructures

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Daniela Radu
UU	UU	UU	UU		19b. TELEPHONE NUMBER: 302-857-6553

Report Title

Final Report: Benchtop Transmission Electron Microscope (TEM) with Electron Diffraction (ED) and Scanning Electron Microscopy (SEM) Capabilities for Analysis of Inorganic Solution-Processed Flexible Solar Cells

ABSTRACT

The award W911NF-14-1-0071 made to Delaware State University enabled the acquisition of a benchtop low-voltage Transmission Electron Microscope (TEM) with Scanning Electron Microscope (SEM) Capability: LV EM 5. The instrument acquisition supports Analysis of Inorganic Solution-Processed Flexible Solar Cells and has been used to accomplished the project objectives:
O1. Support the project "Novel Thin-Film Photovoltaic Technologies Using Solution Nano-Precursors to Cu2ZnSnS4, Fe2SiS4, and Fe2GeS4-Based Absorber Layers", research ongoing in Dr. Daniela Radu's (PI) laboratory.
O2. Build strength in nanotechnology-related research and education at DSU.
The project resulted in two presentations at the National American Chemical Society Meeting, March 20-24, 2015 in Denver, CO.
The instrument was critical to achieve high throughput analysis of nanoparticles used in solution processed thin-films. The LV EM 5 has been used in TEM mode for nanoparticles size screening. SEM mode has been used to identify silica nanostructure morphologies and packing on a analysis stub.
Three students and two faculty members have been trained and are using the instrument since installation and training sessions in November 2014.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received	Paper

TOTAL:

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received	Paper

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

Chalcogenide nanostructured precursors in fabrication of polycrystalline absorber layers in thin-film photovoltaics
View Session Detail

Author: Daniela Radu
Chemistry, DELAWARE STATE UNIVERSITY, Dover, Delaware, United States

Abstract:Chalcogenide semiconductors, such as copper indium gallium diselenide – Cu(In,Ga)Se2 (CIGS), kesterites – Cu2ZnSn(S,Se)4, (CZTS), and recently proposed iron chalchogenide, Fe2SiS4 and Fe2GeS4, offer bandgaps close to ideal for the absorber material in thin-film photovoltaic (PV) technologies. Progress is continuously made in this arena both in terms of small cell efficiencies and in terms of larger area module efficiencies. Besides the cost aspect on Earth applications, chalcogenide solar cells are also interesting for space applications because of their excellent stability against particle irradiation and development of high efficiency flexible cells. Roll-to-roll printed nanoparticle technologies for flexible solar cells could offer the combination of fast, atmospheric pressure deposition, a lightweight substrate, and a thin, inexpensive absorber layer, each of which decreases the cost and the weight of the final solar cell or module, toward making solar energy affordable. Nanoparticles-originated polycrystalline layers of Cu2ZnSn(S,Se)4, (CZTS), and Fe2SiS4 and Fe2GeS4 from nanoparticles synthesis to the solar cell performance will be reviewed.

Number of Presentations: 1.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received	Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received	Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received Paper

TOTAL:

Number of Manuscripts:

Books

Received Book

TOTAL:

Received Book Chapter

TOTAL:

Patents Submitted

Patents Awarded

Awards

Delaware State University, College of Mathematics, Natural Sciences and Technology (CMNST) Excellence in Research Award, 2014

Graduate Students

NAME	PERCENT_SUPPORTED

FTE Equivalent:
Total Number:

Names of Post Doctorates

NAME	PERCENT_SUPPORTED

FTE Equivalent:
Total Number:

Names of Faculty Supported

NAME	PERCENT_SUPPORTED

FTE Equivalent:
Total Number:

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED

FTE Equivalent:
Total Number:

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields: 0.00

Names of Personnel receiving masters degrees

NAME

Total Number:

Names of personnel receiving PHDs

NAME

Total Number:

Names of other research staff

NAME PERCENT_SUPPORTED

FTE Equivalent:
Total Number:

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

See Attachment

Technology Transfer

1. Foreword

The LV EM 5 Transmission Electron Microscope (TEM) with Scanning Electron Microscope (SEM) and electron diffraction (ED) capability was purchased under grant W911NF-14-1-0071 as part of the Research and Education Program for Historically Black Colleges and Universities and Minority-Serving Institutions (HBCU/MI) Equipment/Instrumentation program (Broad Agency Announcement W911NF-13-R-0008, Fiscal Year 2013) and has enhanced the sustainable materials lab capabilities in the Department of Chemistry at Delaware State University. The state-of-the-art low voltage benchtop microscope has arrived at DSU in November 2014. This report reflects the activities that have been supported by the instrument in the period November 2014-January 2015.

The purchase price was $188,000.00 and the installation was completed in a timely manner immediately after equipment delivery.

2. List of Appendices, Illustrations and Tables (if applicable)

TEM images (1.a through 1. c)

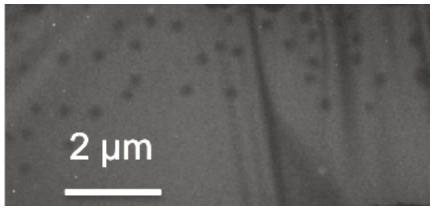

Figure 1.a TEM image of Fe_2GeS_4 on low voltage

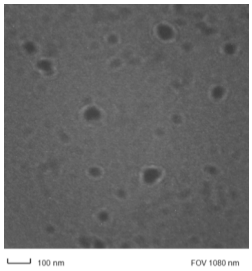

Figure 1.b TEM image of Fe_2GeS_4 on low voltage

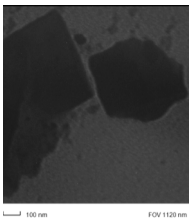

Figure 1.c TEM image of Fe_2GeS_4 on low voltage

SEM images (2.a through 2.b)

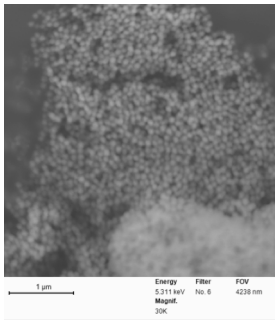

Figure 2.a SEM image of NSN-6 silica nanospheres on low voltage

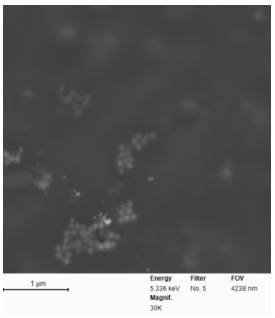

Figure 2.b SEM image of NSN-7 silica nanospheres on low voltage

3. Statement of the problem studied

The analytical capabilities of our laboratory since the purchase of the LV EM 5 increased. Quick screening of samples can now be performed in a timely manner. The instruments enabled analysis (imaging) of the nanostructured materials subject of our study to the extent that it become a routine job. Having a benchtop TEM/SEM in house means that the students have been able to operate the instrument, which speaks to their training; travel to University of Delaware (40 miles) is no longer required only for High Resolution imaging (HR-TEM or SEM) which is needed only for samples that need extensive characterization. The unique feature of the LV EM 5 is that the samples are analyzed in Back Scattered Light and therefore no special coating is required.

Our nanomaterials, presently studies Fe_2GeS_4 are employed to fabricate printed solar cells from nanoparticles precursors.[1]

4. Summary of the most important results

It is of paramount importance that each batch of ink formulated with the nanoparticles contains same particle size distribution. While composition and purity is easy to identify with X-Ray powder diffraction, the particle size cannot be easily analyzed. Therefore, LV EM 5 made a big difference on fast throughput sample characterization and increased our productivity as the analysis is done as soon as the particles are synthesized. Sample TEM images are presented in section 2, images 1.a through 1.c depicting particles on a Cu grid , with particle size distribution easy to observe.

A second project supported by the LV EM 5 requires synthesis and characterization of silica nanospheres. [2]The project, lead by Dr. Cheng-Yu Lai, is focusing on fabrication of nanostructured scaffolds for catalysis in biofuels and other applications. The nanospheres, with particles sizes in the submicron to micron size,

are imaged by LV EM 5 in SEM mode. The SEM images, as showed in Figures 2. a and 2.b are indicative of uniform size distribution which is the information needed by researchers to validate further the packing capabilities in reactors that are tested for biofuels fabrication.

5. References

1. Orefuwa, S. A.; Lai, C.-Y.; Dobson, K.; Ni, C.; Radu, D., Novel Solution Process for Fabricating Ultra-Thin-Film Absorber Layers in Fe₂SiS₄ and Fe₂GeS₄ Photovoltaics. *MRS Online Proceedings Library* **2014,** *1670*, null-null M3 - 10.1557/opl.2014.507.

2. Lai, C.-Y. W., Chia-Wen; Radu, Daniela R.; Trewyn, Brian G. ; Lin, Victor S.-Y., Reversible Binding and Fluorescence Energy Transfer Between Surface-Derivatized CdS Nanoparticles and Multi-Functionalized Fluorescent Mesoporous Silica Nanospheres. *Studies in Surface Science and Catalysis* **2008,** *170B*, 1827-1835.